

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

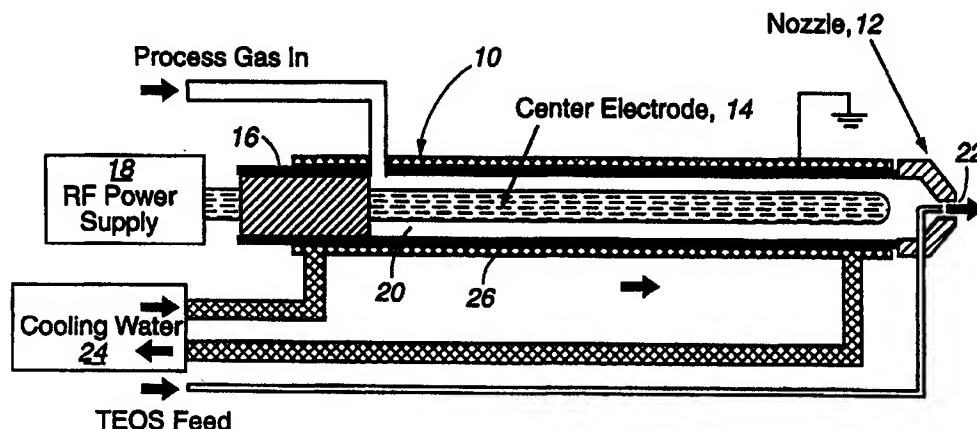
English Equivalent  
for EP 1 090 159



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : <b>C23C 8/00, 16/00, H05H 1/24</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 99/20809</b> (43) International Publication Date: 29 April 1999 (29.04.99)</p>
<p>(21) International Application Number: PCT/US98/22306 (22) International Filing Date: 20 October 1998 (20.10.98) (30) Priority Data: 60/062,822 20 October 1997 (20.10.97) US (71) Applicant: THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; LC/BPL, Los Alamos National Laboratory, MS D412, Los Alamos, NM 87545 (US). (71)(72) Applicants and Inventors: BABAYAN, Steve, E. [US/US]; 6182 Pacemont Drive, Huntington Beach, CA 92648 (US). SELWYN, Gary, S. [US/US]; 2210 Miguel Chavez Road 1114, Santa Fe, NM 87505 (US). HICKS, Robert, F. [US/US]; 10624 Rochester Avenue, Los Angeles, CA 90024 (US). (74) Agent: FREUND, Samuel, M.; LC/BPL, Los Alamos National Laboratory, MS D412, Los Alamos, NM 87545 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>

(54) Title: DEPOSITION OF COATINGS USING AN ATMOSPHERIC PRESSURE PLASMA JET



(57) Abstract

The use of a non-thermal source which is capable of operation at 760 torr is demonstrated. As an example of the application of the present invention, a helium/oxygen gas mixture is introduced into the annular region (20) between two coaxial electrodes (14) driven by a 13.56 MHz radio frequency (RF) source (18) at between 40 and 500 W to produce a stable plasma jet. As detected by optical emission spectroscopy (OES), a high flux of metastable oxygen and no ions are present at the exit of this plasma jet. Silicon dioxide films are deposited by introducing tetraethoxysilane (TEOS) into the effluent stream. A deposition rate of 3020  $\pm$  250 Å/min. is achieved with an RF power of 400 W, 0.2 torr of TEOS, 11.1 torr of oxygen, 748.7 torr of helium, and a total gas flow rate of 41 L/min.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## DEPOSITION OF COATINGS USING AN ATMOSPHERIC PRESSURE PLASMA JET

### FIELD OF THE INVENTION

The present invention relates generally to plasma-enhanced, chemical vapor deposition of coatings and, more particularly, to the use of an atmospheric-pressure, plasma discharge jet for deposition of films on substrates. This invention was made with government support under Contract No. W-7405-ENG-36 awarded by the U.S. Department of Energy to The Regents of the University of California. The government has certain rights in the invention.

### BACKGROUND OF THE INVENTION

Silicon dioxide is one of the primary materials used in integrated circuit production. Silicon dioxide films are used for inter layer dielectrics and gate oxides for transistors and are presently either grown by thermal oxidation of silicon or deposited by thermal or plasma-enhanced, chemical vapor deposition. Plasma-enhanced, chemical vapor deposition (PECVD) is often preferred since deposition temperatures are considerably lower than other methods.

The use of silane to deposit silicon dioxide films has been studied in detail. However, PECVD of silicon dioxide using tetraethoxysilane (TEOS) has been found to have several advantages over silane-based CVD processes. Although higher deposition rates are achieved with silane, better conformal coverage of device is obtained with TEOS due to its lower reactive sticking probability on surfaces (0.045 compared to 0.35 for silane). In addition, TEOS is less hazardous and easier to handle when compared with silane. With the increasing importance of smaller features, step coverage has become an important issue as well. Thus, TEOS has become the primary material for multilevel interconnects in very large-scale, integrated circuit (VLSI) applications. Thermal CVD of silicon dioxide is often carried out with TEOS and Ozone. In this process, the deposition is believed to result from

the reaction of TEOS and O or O<sub>3</sub> in the gas phase. The atomic oxygen is maintained by the decomposition of O<sub>3</sub>. Plasma-enhanced, chemical vapor deposition of SiO<sub>2</sub> is currently performed using TEOS and a reactive oxygen source which contains O atoms or O<sub>2</sub><sup>+</sup> ions.

5           Conventional, low-pressure plasma discharges produce ions and atomic species which may damage underlying layers during the film deposition process. Since atmospheric operation offers certain advantages over vacuum processes, we decided to explore whether the plasma jet could be used for PECVD of SiO<sub>2</sub>.

10           Accordingly, it is an object of the present invention to generate an intense flux of metastable and radical species for use in plasma-enhanced, chemical vapor deposition onto a substrate without exposing the substrate to ionic and atomic species.

          Another object of the invention is to generate an intense flux of metastable and radical species for use in plasma-enhanced, chemical vapor deposition onto a substrate at atmospheric pressure.

15           Yet another object of the present invention is to generate an intense flux of metastable and radical species for use in plasma-enhanced, chemical vapor deposition onto a substrate at atmospheric pressure without significantly heating the substrate.

20           Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

#### SUMMARY OF THE INVENTION

25           To achieve the foregoing and other objects and, in accordance with the purposes of the present invention as embodied and broadly described herein, the method for depositing a material on a substrate hereof may include the

30

steps of: generating reactive species in an arcless, atmospheric-pressure, RF plasma discharge in a gas flowing through an annular region between an electrically conducting chamber having a closed end and an open end and a central electrode located within the chamber and disposed such that the annular region is defined therebetween, whereby the reactive species flow toward the open end of the chamber; introducing a gaseous precursor species of the material into the reactive species in the region of the open end of the chamber, the precursor species being chosen such that it reacts with at least one of the reactive species, the reaction products thereof exiting the open end of the chamber as part of a gaseous atmospheric pressure jet; and placing the substrate in the path of the gaseous jet, whereby the reaction products generate a film of the material on the substrate.

Preferably, substantially all ions produced in the atmospheric-pressure, plasma discharge are consumed in the discharge before the gaseous jet containing the material exits through the open end of the chamber.

In another aspect of the present invention, in accordance with its objects and purposes, the apparatus for depositing a material onto a substrate hereof may include: an electrically conducting chamber having a closed end and an open end; a central electrode located within the chamber defining thereby an annular region; means for flowing gases through the annular region; means for supplying RF energy to either of the central electrode or the electrically conducting chamber such that a continuous plasma discharge occurs between the electrode and the chamber, whereby reactive species are generated which flow toward the open end of the chamber; means for introducing a gaseous precursor species of the material into the reactive species in the region of the open end of the chamber, the gaseous precursor species being chosen such that the precursor species reacts with at least one of the reactive species, whereby a gaseous jet capable of forming the material exits through the open end of the chamber.

It is preferred that the central electrode is disposed collinear with the axis of the chamber.

It is also preferred that the electrode has longitudinal slots therein, each slot having a chosen width and a chosen depth.

5 Preferably also, substantially all ions generated in the atmospheric-pressure, plasma discharge are consumed therein before the gaseous jet containing said material exits through the open end of said chamber.

Benefits and advantages of the present invention include the generation of an intense beam of the material to be deposited without exposing the substrate to ions and atomic species and to a high-temperature source.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form a part of the specification, illustrate the embodiments of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

15 FIGURES 1a-c illustrate the atmospheric-pressure, plasma jet of the present invention, Fig. 1a showing a cross sectional view of thereof, with Figs. 1b and 1c illustrating the side view and the axial cross section of the center electrode thereof.

20 FIGURE 2 shows the effect of RF power and TEOS partial pressure on the  $\text{SiO}_2$  deposition rate.

FIGURE 3 shows the  $\text{SiO}_2$  deposition rate as a function of substrate temperature.

25 FIGURE 4 shows the effect of helium flow rate on the deposition rate of  $\text{SiO}_2$  and on the ozone concentration.

FIGURE 5 shows the concentration of metastable oxygen and of ozone as a function of the distance from the center electrode.

30 FIGURE 6 shows the effect of oxygen partial pressure on the deposition rate and on the  $\text{O}_2(b^1\Sigma_g^+)$  intensity.

FIGURE 7 shows FT-IR absorption spectra of SiO<sub>2</sub> films deposited at different substrate temperatures.

FIGURE 8a shows an AFM image of an SiO<sub>2</sub> film deposited for 10 min. at 115 °C, while FIGURE 8b shows an AFM image of an SiO<sub>2</sub> film deposited for 10 min. at 350 °C.

#### DETAILED DESCRIPTION OF THE INVENTION

Briefly, the present invention utilizes a plasma discharge sustained at atmospheric pressure and near room temperature to deposit films on substrates. A feed gas containing helium and oxygen is caused to enter the annular region between two coaxial electrodes and produces a stable atmospheric pressure plasma jet (APPJ). The jet differs from conventional low-pressure plasma sources in that it produces an intense flux of metastable and radical species instead of ions and atomic species. While ions and atomic species are generated inside the APPJ, they are rapidly consumed by collisions before exiting the space between the electrodes. As an example of the coating process of the present invention, tetraethoxysilane (TEOS), an SiO<sub>2</sub> precursor species which reacts with metastable oxygen, is introduced into the flux thereof in helium gas outside of the space between the electrodes, generating thereby a substantial concentration of SiO<sub>x</sub> species. These species generate an SiO<sub>2</sub> film upon impinging on a silicon substrate. The absence of ions and atoms eliminates the possibility of damaging the underlying layer of the substrate during deposition.

Reference will now be made in detail to the present preferred embodiments of the present invention examples of which are illustrated in the accompanying drawings. Turning now to the Figures, Figs. 1a and 1b are schematic representations of side views of the assembled APPJ of the present invention and the center electrode thereof, respectively, which is used to deposit silicon dioxide and other films onto substrates. The APPJ consists of two concentric electrodes made of stainless steel. Figure 1c is a schematic representation of the axial cross section of the center electrode showing the

longitudinally placed slots or flutes therein. In one embodiment, each identical flute has a width dimension and a depth dimension, typically between 0.02 and 0.1 in. It is preferred that the ratio of the width dimension to the depth dimension of the flutes is approximately one-to-three. The use of  
5 such slots has been found to produce an enhanced plasma density that provides a broader operating window without arcing than for the same conditions using a solid, center electrode; that is, the apparatus can operate over a wider He/O<sub>2</sub> mixture range and at higher RF power without arcing. Radio frequency power at 13.56 MHz was applied to the inner electrode.  
10 Unlike atmospheric pressure glow discharges, the APPJ does not require a dielectric material between the electrodes to create a stable plasma. The inner (center) electrode employed had a diameter of 0.50", while the outer electrode had an inner diameter of 0.62". Oxygen and helium gas flow rates were measured with rotameters and the gases were mixed before entering  
15 the annular space between the two electrodes. The TEOS carrier gas, helium, was regulated by a mass flow controller. This carrier gas was bubbled through a reservoir of TEOS at a fixed temperature. The resulting mixture was combined with the flowing plasma gases inside a nozzle placed at the open end of the jet. This nozzle directed the effluent flow toward the  
20 substrate to be coated.

The SiO<sub>2</sub> films were deposited on *p*-type silicon wafers which were placed 1 to 3 cm away from the nozzle. Prior to deposition, the silicon wafers were first cleaned in boiling sulfuric acid, and subsequently immersed in dilute hydrofluoric acid for 30 seconds. After a thorough rinse, the substrates were  
25 placed on a sample holder disposed in front of the jet and a temperature between 85 and 350°C was chosen and maintained. Temperature measurements were made using a thermocouple placed 1 mm behind the sample surface. After the temperature had stabilized, the helium and oxygen flow rates were established and the RF power between 75 and 500W was  
30 applied to the electrodes forming a stable discharge. Flow of the TEOS



carrier gas was then initiated, allowing the TEOS/helium mixture to combine with the effluent stream. Unless otherwise noted, the standard process conditions were:  $P_{\text{He}} = 757.2\text{torr}$ ,  $P_{\text{O}_2} = 2.8\text{torr}$ ,  $P_{\text{TEOS}} = 7.1\text{mtorr}$ , total flow rate = 49.4 L/min,  $T_{\text{substrate}} = 115^\circ\text{C}$ , nozzle to sample distance = 1.7 cm, RF power = 280W. After deposition, the films were analyzed to assess their quality.

Optical emission spectroscopy (OES) was used to detect the presence of oxygen atoms, ions, and metastables outside of the jet. The emission detector was disposed and focused perpendicular to the effluent stream. In addition, ozone concentrations were measured by an electrochemical gas monitor. The gas monitor was connected to a 1/16" stainless steel tube placed into the exiting gas stream (not shown in Figs 1 a-c hereof). This allowed for continuous sampling of the effluent stream as the process conditions were changed. After deposition, the film composition was analyzed by infrared spectroscopy, the film thickness and the refractive index were measured by ellipsometry, and the surfaces were imaged by atomic force microscopy. The dielectric constant was also calculated from capacitance data by constructing a parallel plate capacitor of known plate area and separation.

Having generally described the invention, the following examples provide more detail:

#### EXAMPLE 1

The effects of the TEOS partial pressure and the RF power on the deposition rate are shown in Figure 2. The TEOS partial pressure was varied from 1 to 8 mtorr and RF power levels were between 180 and 500 W. At an RF power of 500 watts, the temperature of the sample holder (not shown in Figs. 1a-c hereof), which was located 1.5 cm away from the nozzle, was found not to rise above  $115^\circ\text{C}$ . This demonstrates the non-thermal nature of the APPJ. The log-log representation of the data shown in Fig. 2 indicates that the reaction order for the TEOS partial pressure is 0.47, whereas the reaction order for the RF power is 1.41. The reaction order for the RF power

was found to be the largest of any process variable, while the second largest contribution to the deposition rate derives from the TEOS partial pressure. By increasing both the TEOS partial pressure to 0.2 torr and the RF power to 400 W, silica films were grown at  $3020 \pm 250 \text{ Å/min}$ . It is believed by the present  
5 inventors that this value may be limited by the small bubbler which can only receive 200 sccm of the carrier gas.

An increase in the sample temperature with all other process conditions held constant shows a decrease in the deposition rate. Without additional heating of the sample, a temperature of  $107^\circ\text{C}$  was maintained by  
10 the presence of the plasma at the standard operating conditions. A plot of the logarithm of the deposition rate as a function of  $1000/T$  is shown in Fig. 3. The plot is not linear indicating the departure from the Arrhenius form.

The gas mixture entering the APPJ is primarily composed of helium. The helium flow rate was typically 49 L/min. The effect of the deposition rate  
15 on the helium flow is shown in Fig. 4. A maximum is obviously present at 40.2 L/min. The decrease in ozone concentration with increasing helium flow rate is also shown in Fig. 4 for comparison. The deposition rate and ozone concentration as functions of helium flow rate show no correlation.

As shown in Fig. 5, the metastable oxygen intensity decays with  
20 increasing distance from the jet. Axial analysis of the effluent stream with OES has shown that metastable oxygen ( $b^1\Sigma_g^+$ ) is the dominant reactive species. The intensity reported in this Figure was found by summing the area under the metastable oxygen peaks located between 758 and 761 nm. This intensity is approximately 10,000 times greater than that for atomic oxygen.  
25 The metastable species persist for more than 2 cm beyond the jet, whereas the weak atomic oxygen signal is only present within 1.5 cm of the jet. Figure 5 also shows the increase in ozone concentration with distance. For this data, a long nozzle was constructed to extend the outer electrode 4.2 cm beyond the center electrode. This permitted the detection of ozone at varying  
30 distances without the dilution effect from the expansion of the jet stream as it

exits the nozzle. The effect of the introduction of TEOS at different axial distances was then correlated with the axial flux profiles of metastable oxygen and ozone outside the APPJ. To determine whether it is the  $O_3$  or the  $O_2(b^1\Sigma_g^+)$  that is responsible for the gas-phase dissociation of TEOS, the TEOS was introduced at two different distances from the center electrode as indicated in Fig. 5. In both cases, the substrate was 1.7 cm away from the TEOS feed. The deposition rate for Case I, where the TEOS feed was placed 1.1 cm from the center electrode, was twice that of Case II, where the TEOS feed was placed at 3.7 cm and the ozone concentration was high. As stated hereinabove, the  $SiO_2$  is formed once the reaction products have been deposited onto the silicon substrate.

Figure. 6 shows the effect of the oxygen partial pressure on the deposition rate. For this Figure, the oxygen was passed through the plasma jet. This data indicates that the reaction order for oxygen is 0.28. Oxygen must be present for the reaction to proceed. This differs from an atmospheric-pressure glow discharge, which can deposit silicon dioxide in a helium plasma without the presence of oxygen. As shown in Fig. 6, the  $O_2(b^1\Sigma_g^+)$  signal intensity decreases with increasing oxygen partial pressure. This trend is opposite that of the deposition rate dependence on the oxygen partial pressure. In other experiments, oxygen was introduced only through the nozzle where the TEOS was introduced. When the oxygen is delivered in this manner, metastable oxygen is not produced. Introducing the oxygen through the nozzle only, results in deposition rates that are less than one-tenth of the rates achieved when the same amount of oxygen is passed through the plasma jet.

The infrared spectra in Fig. 7 show the effect of temperature on the film quality. The Si-O-Si asymmetric stretching, bending, and rocking modes are observed at 1080, 800, and 450  $cm^{-1}$ , respectively. The absorption due to Si-O-H is observed at 3650  $cm^{-1}$ . Hydrogen bonding between Si-O-H and  $H_2O$  is observed at 3400 and 930  $cm^{-1}$ . The peaks located at 3650, 3400,

and  $930\text{ cm}^{-1}$  all decrease with increasing growth temperature. The CH stretching mode at  $2900\text{ cm}^{-1}$  and the C=O stretching mode at  $1730\text{ cm}^{-1}$  were not observed.

5 The films deposited at  $115^{\circ}\text{C}$  have  $0.1\text{-}0.3\text{ }\mu\text{m}$  circular features on the film surface. Figure 8a shows an atomic force microscope image of such a surface. The white regions represent material protruding out of the plane of the deposited film. The peak-to-valley roughness is approximately  $2300\text{ }\text{\AA}$ . The z-axis is magnified by a factor of 5 to emphasize these surface features. Figure 8b shows an atomic microscope image for a film deposited at  $350^{\circ}\text{C}$ .  
10 The surface is featureless. The peak-to-valley roughness is approximately  $20\text{ }\text{\AA}$ .

The refractive index squared, measured by ellipsometry, did not show a significant change from sample to sample. The square of the refractive index was  $1.45 \pm 0.02$  for most samples. To better assess the film quality, the dielectric constant was calculated from capacitance data for several films  
15 deposited by this process. From capacitance data, the dielectric constants were found to range from  $5.0 \pm 0.2$  for films deposited below  $150^{\circ}\text{C}$  to  $3.81 \pm 0.03$  for films deposited at  $350^{\circ}\text{C}$ , indicating that excellent dielectric properties are attainable.

20 Both the high flow velocity and the use of helium, which limits ionization, prevents arcing in the APPJ. Figure 4 shows that the deposition rate reaches a maximum with a helium flow rate of  $40.2\text{ L/min}$ . Although the oxygen and TEOS partial pressures were not constant in Fig. 3, the maximum is a result of the balance between the production of reactive species in the plasma stream, and the residence time of the TEOS in the plasma stream.  
25 Below this point, the number of reactive species produced within the plasma decreases. At  $50\text{ L/min}$  of helium, the linear velocity exiting the jet is greater than  $26\text{ m/s}$ . This does not provide sufficient time for the gas-phase reaction to occur before the substrate,  $2\text{ cm}$  away, is reached. The slow decay of the  
30 curve with increasing helium flow rate is evidence of the effect of the TEOS

residence time in the plasma.

The plasma can be sustained at approximately 40 watts of forward power. With the present APPJ design, application of an RF power exceeding 500 watts generally produces arcing which can physically damage the electrodes. The large value of 1.41 for the slope of the log-log plot of the deposition rate as a function of the RF power confirms the strong dependence of the deposition rate on the amount of reactive species generated by the APPJ. The increase of the deposition rate with increasing power indicates that complete conversion is not achieved. This demonstrates the role of the collision frequency between the TEOS and the reactive species on the deposition rate, since increasing the power increases the concentration of reactive species in the jet effluent.

The dependence of the deposition rate on the helium flow rate, applied RF power, and TEOS flow rate all demonstrate that the deposition process is limited by gas-phase reactions in the plasma stream. However, upon increasing the substrate temperature, the deposition rate decreases substantially. Chemical vapor deposition using TEOS and oxygen is characterized by a negative activation energy. The deposition process is known to be exothermic. Additionally, increasing the substrate temperature will shift the adsorption equilibrium to the left. It is believed by the present inventors that the exothermic nature of the surface reaction and decrease in the effective adsorption of the TEOS on the substrate surface likely both contribute to the positive slope observed in Fig. 3. Films deposited at low temperatures are less dense. Since the deposition rate was measured from the film thickness, the deposition rate of these less-dense films will appear slightly higher than the more dense films grown at higher temperatures. This difference impacts the plot shown in Fig. 3 by slightly reducing the curvature.

As stated hereinabove, the APPJ effluent contains no ions. At atmospheric pressure, the ions are rapidly consumed upon exiting the annular space between the electrodes. Thus, helium metastables, oxygen atoms,

ozone, or oxygen metastables are the only reactive species which could be responsible for the gas phase decomposition of the TEOS. The measured atomic oxygen concentration outside the APPJ is too small to contribute significantly to the deposition rate. The present inventors believe that helium metastables are not directly responsible for the gas phase decomposition of TEOS, since deposition is not observed without the presence of oxygen. In a helium APG process, without the addition of oxygen, silicon dioxide is deposited using TEOS as both the silicon and oxygen source. The lack of correlation between the deposition rate and ozone concentration illustrated in Figs. 4 and 5 hereof indicates that ozone plays little if any role in the deposition process using the atmospheric pressure plasma jet.

The discussion set forth hereinabove suggests that metastable  $O_2(b^1\Sigma_g^+)$  or  $O_2(a^1\Delta_g^+)$ , is responsible for the gas-phase decomposition of TEOS which drives the deposition process. The ten-fold decrease in the deposition rate when oxygen is introduced only into the nozzle, in which metastable oxygen is not produced, is evidence of the important role of metastable oxygen in the reaction mechanism. As shown in Fig. 5 some correlation exists between the  $O_2(b^1\Sigma_g^+)$  intensity and the deposition rate with increasing distance from the jet. However, the data presented in Fig. 6 indicates that the  $O_2(b^1\Sigma_g^+)$  intensity decreases with increasing oxygen partial pressure yet the deposition rate increases with increasing oxygen partial pressure. Optical emission spectroscopy does not give a quantitative measure of the species present; rather, it detects electronic transitions. Thus, it cannot be determined that the  $O_2(b^1\Sigma_g^+)$  concentration has the same trend as the detected intensity, or that  $O_2(b^1\Sigma_g^+)$  plays no role in the deposition process. It is likely that the  $O_2(a^1\Delta_g^+)$  metastable state may be the active species present in the jet effluent, since previous work in solutions and gas mixtures by others have shown that the consumption of  $O_2(b^1\Sigma_g^+)$  by chemical reaction is insignificant when compared to deactivation to produce  $O_2(a^1\Delta_g^+)$  in solution.

Generally, increasing the temperature and incorporating H<sub>2</sub> into the gas stream increases the film quality by removing carbon and hydroxyl groups from the film. The increase in growth temperature reduces the hydroxyl concentration in the films, as may be observed from the infrared spectra of Fig. 7. The peaks located at 3650, 3400, and 930 cm<sup>-1</sup> all decrease with increasing deposition temperature. The CH and C=O stretching vibrations are not present in the infrared spectra collected for any of the films deposited. However, it should be mentioned that upon addition of an amount as small as 0.25% of hydrogen, no deposition occurred even after 20 minutes.

Undesirable surface features were observed on the films deposited by the APPJ when the substrate temperature was maintained at 115 °C. The AFM image shown in Fig. 8a reveals surface defects due to voids within the deposited silicon dioxide film. As shown in Fig. 8b, films deposited at 350 °C were smooth, suggesting the absence of voids. At low substrate temperatures the energy supplied to the surface atoms is too small for significant surface migration. Therefore, the siloxane chains deposited on the substrate may not have sufficient time to arrange. Thus, a void can form around a protruding siloxane chain or cluster. At higher growth temperature the surface migration prevents the voids from forming during deposition. In addition, the shoulder located at 1200 cm<sup>-1</sup>, to the Si-O-Si asymmetric stretching mode increases with decreasing temperature as shown in Fig. 7. This may be from an increase in the porosity of the deposited films. Generally, the dielectric-screening effect reduces the vibration frequency. This effect is diminished near the surface of a large void. The Si-O-Si vibrations facing a large void or the film surface are not subject to the dielectric screening effect, and thus their vibrational frequency is not shifted.

The dielectric constant of silica generally obeys the equation  $\epsilon = 3.8073 + 2.72 \times 10^{-22} \times N$ , where N is the concentration of hydroxyl ions per cubic centimeter. In the limit where no hydroxyl ions are present, such as

in a thermally grown oxide, the dielectric constant will be 3.8073. The measured dielectric constants for the films deposited varied from  $3.81 \pm 0.03$  to  $5.0 \pm 0.2$  indicating hydroxyl concentrations of  $9.93 \times 10^{18}$  and  $4.38 \times 10^{21}$  hydroxyl ions per cubic centimeter, respectively. The increase in the sample temperature promotes the desorption of  $H_2O$  produced in the formation of silicon dioxide from TEOS. However, the increase in temperature reduces the deposition rate. Thus, the deposition rate desired and the dielectric constant required for a particular application are balanced by the substrate temperature.

#### EXAMPLE 2

Suitable precursors for depositing a film containing a metal atom M are  $ML_x$  (where  $L_x$  is a ligand and x is the valence of the metal atom) compounds that are (a) volatile, (b) stable for transport to the nozzle, and (c) decompose without depositing impurities in the film. Suitable precursors may be identified by simple experimentation. Suitable volatile compounds are generally those containing short-chain alkyl groups and alkoxides mentioned hereinbelow. However, halogens (e.g., chlorides), amines, phosphines, and carbonyl ligands are often suitable.

The Table identifies other thin films that should be able to be deposited with the plasma jet of the present invention. In all of these processes, helium will be introduced into the plasma. If an oxide is to be deposited, then  $O_2$  is mixed with the helium and the mixture passed through the plasma. If a nitride is to be deposited, then either  $N_2$  or  $NH_3$  will be mixed with the helium and the mixture passed through the plasma. If a carbide is to be deposited, then either acetylene or methane will be mixed with the helium and the mixture passed through the plasma (other hydrocarbon gases, such as ethane, ethylene, etc. may be used as well).

For deposition of a pure elemental film, hydrogen may be passed through the plasma. The precursor containing the element to be deposited is always introduced into the nozzle following the plasma; otherwise, a film will



be deposited on the electrodes and the plasma will extinguish. If an oxide film is to be deposited, then an alkoxide containing the element to be deposited will be introduced into the nozzle. Alkoxides have the general formula:  $M(OR)_x$ , where  $x$  is the number of alkoxide ligands which is equal to the valence of the metal atom, and  $R$  is an alkyl group attached to the oxygen atom. The alkyl group may include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tertiary butyl, allyl, vinyl, etc.

For depositing nitrides and carbides, an organometallic molecule containing the element to be deposited; i.e.,  $MR_x$ , where  $x$  is equal to the valence of the metal, would be employed. The alkyl group,  $R$ , is the same as described above. For example, to deposit GaN,  $N_2$  and He would be passed through the plasma, and He and  $Ga(CH_3)_3$  introduced into the nozzle. Here the  $R$  group would be a methyl ligand. Other gallium precursors could be used as well; for example,  $Ga(N(CH_3)_2)_3$  may be employed.

TABLE

Film		Precursors and Gases Used
$SiO_2$	Silicon Dioxide	Tetraethoxysilane (TEOS), TEOS/ $O_2$ , $SiH_4/O_2$ , $Si_2H_6/O_2$ .
$Si(NMe_2)_4/O_2$		
$GeO_2$	Germanium Dioxide	$Ge(CH_3)_4/O_2$ , $GeH_4/O_2$ , $Ge(CH_3O)_4/O_2$
$Al_2O_3$	Aluminum Oxide	$Al(OC_2H_5)_3/O_2$ , $Al(C_2H_5O)_3/O_2$
$TiO_2$	Titanium Dioxide	$Ti(C_2H_5O)_4/O_2$ , $Ti(CH_3O)_4/O_2$
$Si_3N_4$	Silicon Nitride	TEOS/ $N_2$ , $SiH_4/N_2$ , TEOS/ $NH_3$ , $SiH_4/NH_3$ , $Si(NMe_2)_4/N_2$
BN	Boron Nitride	$BF_3/N_2$ , $BF_3/NH_3$ , $B(C_2H_5)_3/N_2$ , $B_2H_6/N_2$ , $B_2H_6/NH_3$
GaN	Gallium Nitride	$Ga(C_2H_5)_3/N_2$ , $Ga(C_4H_9)_3/N_2$ , $Ga(CH_3)_3/N_2$ , $Ga(CH_3)_3/NH_3$ , $AlH_3N(CH_3)_2/N_2$ , $Al(CH_3)_3/N_2$ , $AlH(CH_3)_2/N_2$ , $Al(CH_3)_3/NH_3$
AlN	Aluminum Nitride	$Ti(NMe_2)_4$ , $Ti(NMe_2)_4/N_2$ , $Ti(NMe_2)_4/NH_3$ , $TiCl_4/NH_3$
TiN	Titanium Nitride	$In(CH_3)_3/N_2$ , $In(C_2H_5)_3/N_2$ , $In(CH_3)_3/NH_3$ , $In(C_2H_5)_3/NH_3$ , $WCl_6/N_2$ , $WCl_6/NH_3$ , $W(CO)_6/NH_3$ , $W(CO)_6/N_2$
InN	Indium Nitride	TEOS/ $O_2/F_2$ , $SiH_4/O_2/F_2$ , $Si_2H_6/O_2/F_2$
$WN_x$	Tungsten Nitride	TEOS/ $N_2/O_2$ , $SiH_4/N_2/O_2$ , $Si(NMe_2)_4/O_2$
$SiO_2-xF_{2x}$	Silicon oxy-fluoride	$SiH(C_2H_5)_3/C_2H_2$ , $SiH_4/C_2H_2$ , $Si_2H_6/C_2H_2$ , $SiH_4/CH_4$
$SiO_2-xN_{2/3x}$	Silicon oxy-nitride	$Ti(NMe_2)_4/C_2H_2$ , $Ti(NMe_2)_4/CH_4$ , $TiCl_4/CH_4$
SiC	Silicon Carbide	$WCl_6/C_2H_2$ , $WCl_6/CH_4$ , $W(CO)_6$ , $W(CO)_6/C_2H_2$
TiC	Titanium Carbide	$CH_4$ , $C_2H_6$ , $C_2H_4$ , $C_2H_2$
$WC_x$	Tungsten Carbide	$SiH_4$ , $Si_2H_6$ , $SiH_4/H_2$ , $Si_2H_6/H_2$
C	Diamond	
Si*	Silicon*	

Cu	Copper	$\text{Cu}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ , $\text{Cu}(\text{OCH}_2\text{CH}_3)_2$
Al	Aluminum	$\text{AlH}_3\text{N}(\text{CH}_3)_2/\text{H}_2$ , $\text{Al}(\text{CH}_3)_3/\text{H}_2$
W	Tungsten	$\text{WCl}_6/\text{H}_2$ , $\text{W}(\text{CO})_6/\text{H}_2$

\*Polycrystalline silicon, or amorphous hydrogenated silicon.

Other films that can be deposited include metal phosphides (MP, e.g., BP, GaP, AlP, etc.) and metal arsenides (MAs, e.g., AlAs, GaAs, InAs, etc.). These films might be deposited as polycrystalline or amorphous hydrogenated layers. Precursors for zirconium nitride and carbide ( $\text{ZrN}$ ,  $\text{ZrC}$ ) may be identified by substituting Zr for Ti in the compounds in the right-hand column of the TABLE, since zirconium is in the same row of the Periodic Table as titanium. Similarly, precursors for tantalum nitride and carbide ( $\text{TaN}_x$  and  $\text{TaC}_x$ ) may be identified by substitution of Ta for W in the right-hand column of the TABLE. However, since Ta is in the next row to the left of W in the Periodic Table, the same ligands might be used as those for W, except that one fewer ligand would be required; e.g.,  $\text{Ta}(\text{CO})_5$ .

The range of deposition temperatures is 100 to 1000 °C, with a preferable range of 250 to 500 °C.

The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

## WHAT IS CLAIMED IS:

1. A method for depositing a material onto a substrate, comprising the steps of:
  - (a) generating a reactive species in an arcless, atmospheric-pressure, RF plasma discharge in a gas flowing through an annular region  
5 between an electrically conducting chamber having a closed end and an open end and a central electrode located within the chamber and disposed such that the annular region is defined therebetween, whereby said reactive species flow toward the open end of the chamber;
  - (b) introducing a gaseous precursor species of said material into the  
10 reactive species in the region of the open end of the chamber, said gaseous precursor species being chosen such that said precursor species reacts with at least one of said reactive species, whereby a gaseous jet capable of forming said material exits through the open end of the chamber; and
  - (c) placing said substrate in the path of the gaseous jet, whereby;  
15 said material is deposited on said substrate.
2. The method for depositing a material onto a substrate as described in Claim 1, whereby substantially all ions generated in the atmospheric-pressure, plasma discharge are consumed therein before the gaseous jet exits through the open end of the chamber.
3. The method for depositing a material onto a substrate as described in Claim 1, wherein said flowing gas includes an O<sub>2</sub>/He mixture.
4. The method for depositing a material onto a substrate as described in Claim 3, wherein said gaseous precursor species includes tetraethoxysilane, and said material is SiO<sub>2</sub>.

5. The method for depositing a material onto a substrate as described in Claim 3, wherein said substrate is silicon.

6. The method for depositing a material onto a substrate as described in Claim 3, wherein 13.56 MHz RF energy is applied to the central electrode, and the electrically conducting chamber is grounded.

7. An apparatus for depositing a material onto a substrate, which comprises in combination:

(a) an electrically conducting chamber having a closed end and an open end;

5 (b) a central electrode located within said chamber defining thereby an annular region;

(c) means for flowing gases through the annular region;

(d) means for supplying RF energy to either of said central electrode or said electrically conducting chamber such that a continuous plasma  
10 discharge occurs between said electrode and said chamber, whereby reactive species are generated which flow toward the open end of said chamber;

(e) means for introducing a gaseous precursor species of said material into the reactive species in the region of the open end of the chamber, said gaseous precursor species being chosen such that said  
15 precursor species reacts with at least one of said reactive species, whereby a gaseous jet capable of forming said material exits through the open end of said chamber.

8. The apparatus for depositing a material onto a substrate as described in Claim 7, wherein said electrically conducting chamber has a longitudinal axis and said central electrode has a longitudinal axis, and whereby said central electrode is disposed such that the longitudinal axis  
5 thereof is collinear with the longitudinal axis of said chamber.

9. The apparatus for depositing a material onto a substrate as described in Claim 7, wherein said electrode has longitudinal slots therein, each slot having a chosen width and a chosen depth.

10. The apparatus for depositing a material onto a substrate as described in Claim 9, wherein each slot has the same width and the same depth and wherein the ratio of the chosen width to the chosen depth of the slots is approximately one-to-three.

11. The apparatus for depositing a material onto a substrate as described in Claim 9, whereby substantially all ions generated in the atmospheric-pressure, plasma discharge are consumed therein before the gaseous jet exits through the open end of said chamber.

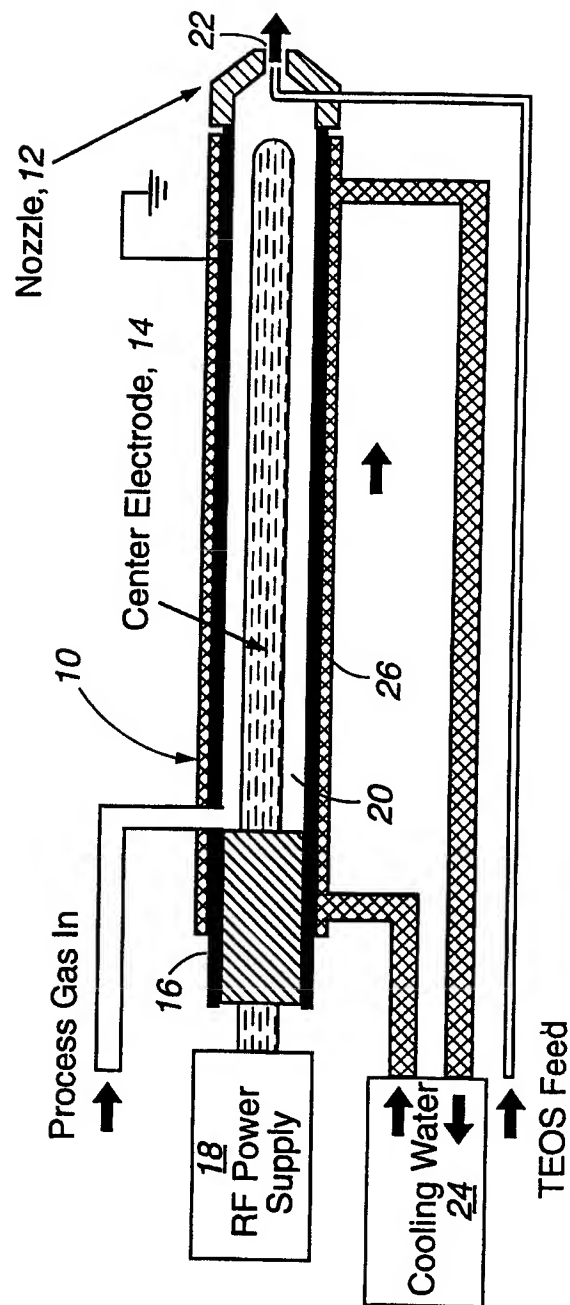
12. The apparatus for depositing a material onto a substrate as described in Claim 9, wherein the flowing gas includes an O<sub>2</sub>/He mixture.

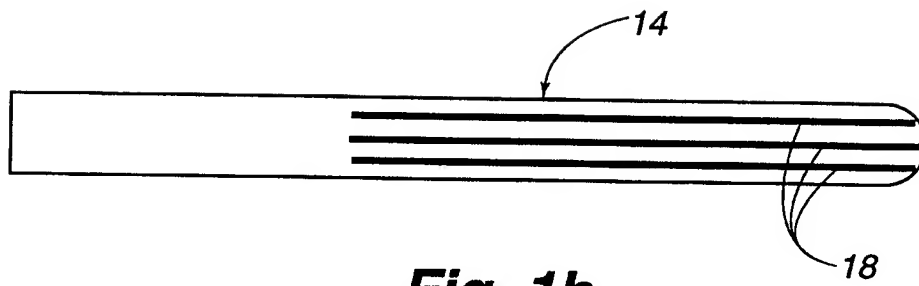
13. The apparatus for depositing a material onto a substrate as described in Claim 12, wherein said gaseous precursor species includes tetraethoxysilane, and said material is SiO<sub>2</sub>.

14. The apparatus for depositing a material onto a substrate as described in Claim 12, wherein 13.56 MHz RF energy is applied to said central electrode, and said electrically conducting chamber is grounded.

15. The apparatus for depositing a material onto a substrate as described in Claim 12, wherein said substrate is silicon.

1/8

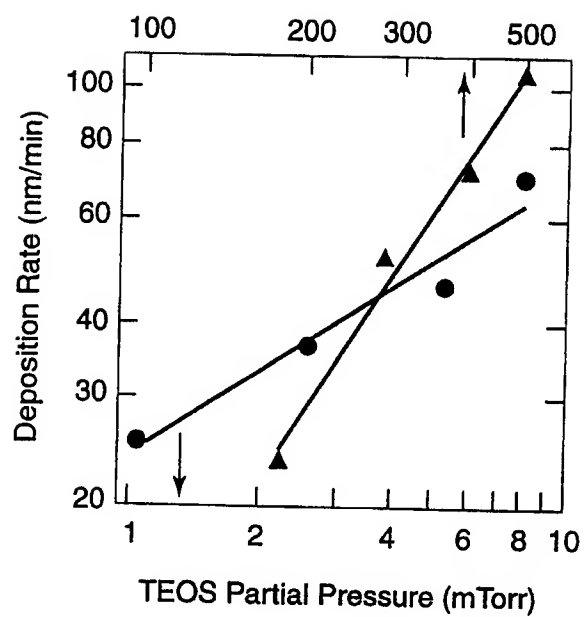
**Fig. 1a**



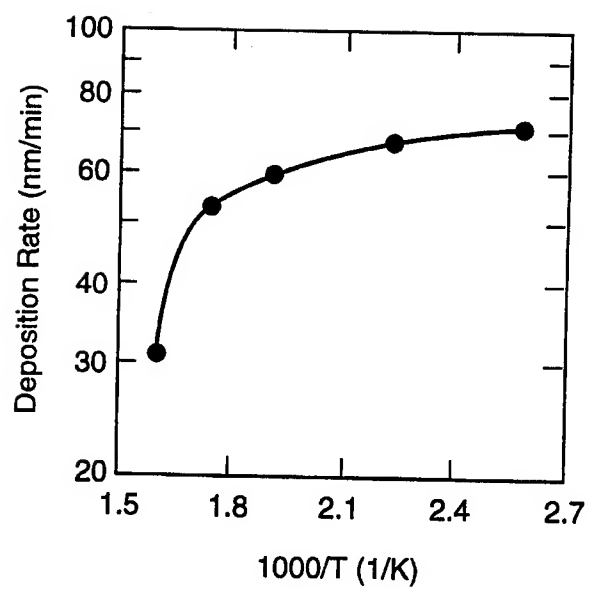
**Fig. 1b**

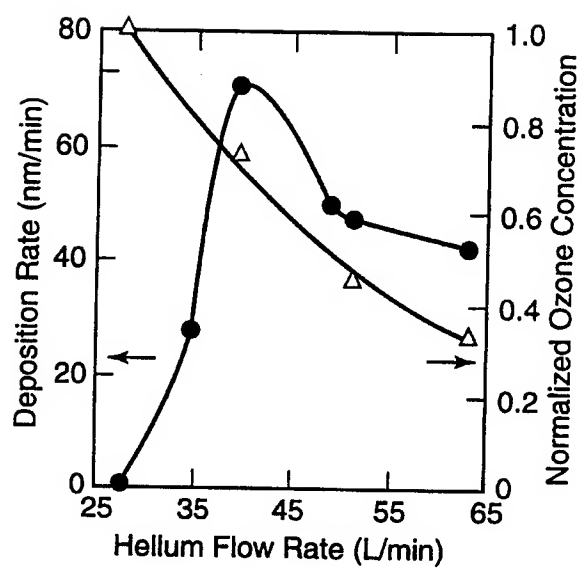


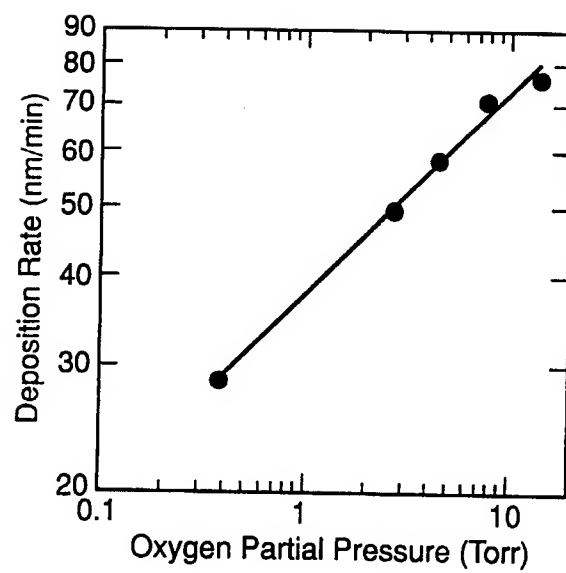
**Fig. 1c**

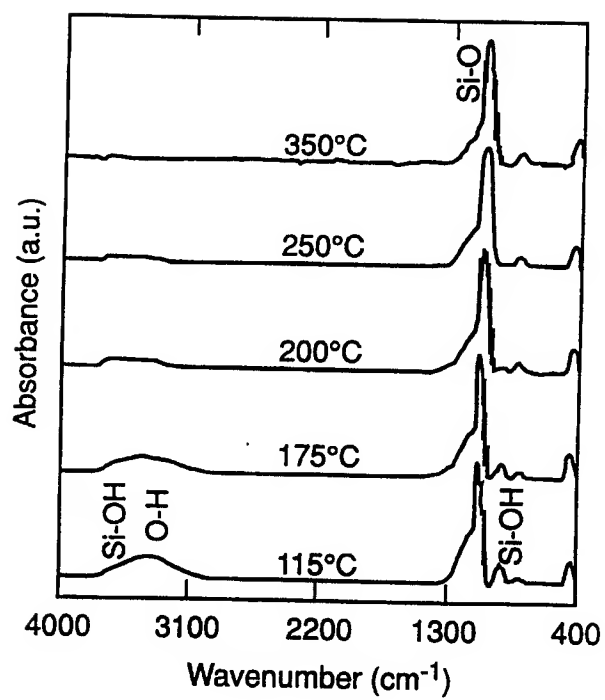
**Fig. 2**

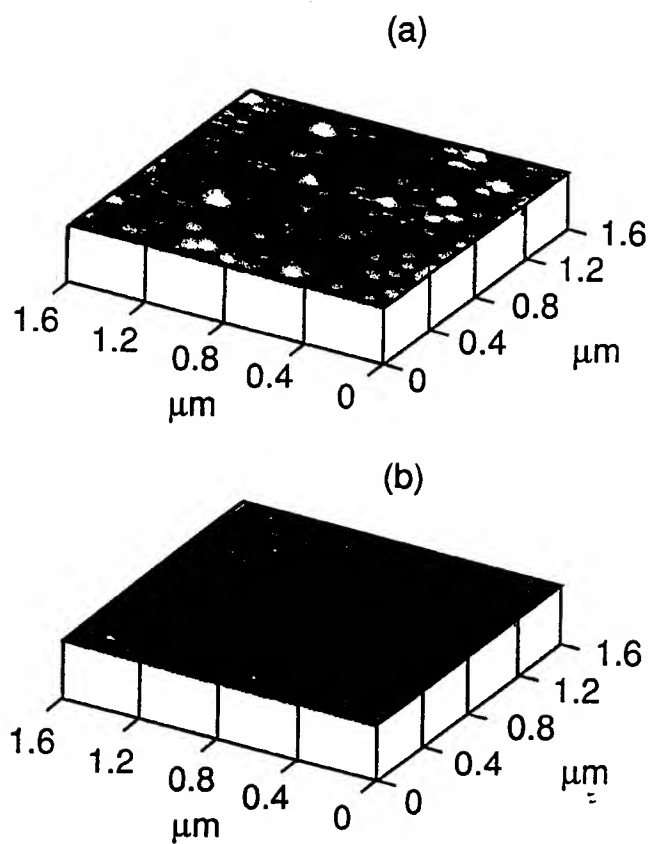


**Fig. 3**

**Fig. 4**

***Fig. 5***

**Fig. 6**

**Fig. 7**

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/22306

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 8/00, 16/00; H05H 1/24

US CL : 118/723R; 427/255.8, 579, 588

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 118/723R; 427/255.8, 579, 588

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NoneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
None

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,648,147 A, (BISCHOF et al.) 07 July 1997 (07-07-97), see entire document.	1-15
A	US 5,370,737 A, (MATHIS) 06 December 1994 (06-12-94), see entire document.	1-15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

27 NOVEMBER 1998

Date of mailing of the international search report

04 JAN 1999

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

Bernard D. Pianalto  
Telephone No. (703) 308-0661